Unidirectional Crystallization of Charged Colloids Driven by Diffusion of Base(Poster session 2, New Frontiers in Colloidal Physics : A Bridge between Micro- and Macroscopic Concepts in Soft Matter)

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シリカ（SiO_2）粒子の表面電荷数は pH とともに増加する。このため、シリカ粒子/水分散系は、pH 増加にともない、“コロイド結晶” 構造を形成する。本研究では、シリカコロイド中にアルカリを拡散させ、生じた pH 勾配のもとでコロイド結晶を一方向成長させた。長さ数 cm に達する巨大な結晶が生成した。結晶成長は、1）シリカ粒子の荷電反応を伴うアルカリ分子の拡散、および 2）シリカコロイドの電荷誘起結晶化、のカップリングにより説明できた。

Charged colloids form ordered “crystal” structures in their dilute dispersions, due to electrostatic interparticle interaction. Here we describe unidirectional crystal growth of charged colloidal silica dispersions, under a *p*H gradient formed by diffusion of a weak base, pyridine (Py)[1]. The crystals consisted of volume-filling pillar-shaped grains, whose height and width were in the order of cm and sub-cm.

Figure 1(a) shows the experimental set-up. Salt-free dispersion of colloidal silica (particle diameter = 110 nm, particle concentration = 3.4 vol%) was introduced into a cell (1×1×4.5 cm) having a semi-permeable membrane on its bottom, and was kept in contact with a 500 ml reservoir of an aqueous solution of Py. The observed crystal growth curves (*h*: crystal height) at four Py concentrations [Py] are shown in Figure 1(b) by symbols.

We previously reported the charge-induced crystallization of colloidal silica with varying *p*H [2]. The silica surface is covered by weakly acidic silanol groups ($\equiv$Si-OH $\rightleftarrows$ $\equiv$Si-O^- + H^+), whose dissociation is enhanced by additions of bases; thus, charge number of the particle increases with *p*H, resulting in the charge-induced crystallization at above a critical *p*H value. When Py molecules are added to the colloidal silica, they partly provide surface charges on the silica particle ($\equiv$Si-OH + Py $\rightarrow$ $\equiv$Si-O^- + PyH^+) due to neutralization reaction; this can be regarded as an electrostatic adsorption. The other part of Py is present in the medium in an undissociated form. Hereafter we denote concentrations of the adsorbed (ionized) and free (undissociated) Pys as *S* and *C*, respectively (shown in Figure 1(a)). Then, the one-dimensional reaction-diffusion equation for $S = S(x, t)$ and $C = C(x, t)$ is given by

$$\partial C / \partial t = [D/(1+\partial S / \partial C)] (\partial^2 C / \partial x^2)$$

where *D* is the diffusion constant of Py.

Based on experimental *S* - *C* relationship, we numerically solved the diffusion equation to obtain $S(x, t)$. Theoretical growth curves were calculated by assuming that the crystallization takes place when $S(x, t)$ reached a critical value for the crystallization which was separately determined for homogeneous system. Figure 1(b) compares the observed and theoretical (solid curves) growths for four [Py]s. They are in close agreements, suggesting that the crystallization was due to coupling between the reaction-diffusion process and charge-induced crystallization.

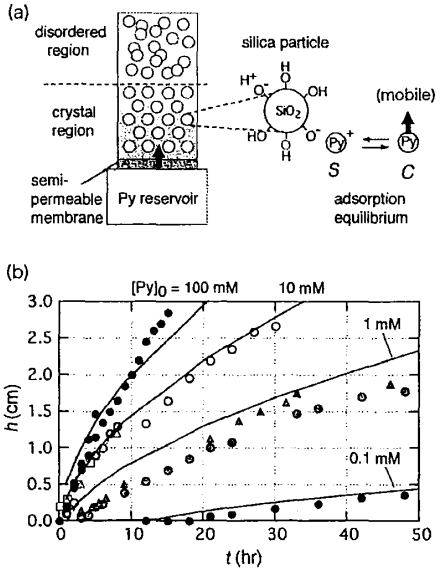

Figure 1. (a) Illustration of the unidirectional crystal growth
(b) Observed and theoretical growth curves.

[1] J.Yamanaka, M.Murai, Y.Iwayama, M.Yonese, K.Ito, T.Sawada, *J. Am. Chem. Soc.* **126**, 7156 (2004); M.Murai, et al., *Langmuir*, in press. [2] J.Yamanaka, H.Yoshida, T.Koga, N.Ise, T.Hashimoto, *Phys. Rev. Lett.* **80**, 5806 (1998).